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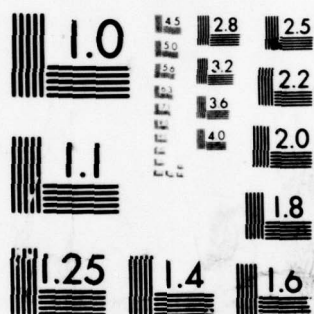


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<p>Scanning transmission electron microscopy (STEM), AES, and ESCA have been used to characterize changes that occur with handling and hydration on aluminum surfaces prepared for adhesive bonding. Three commercial surface treatments were considered - FPL, PAA, and CAA. The resulting surfaces are amorphous aluminum boemite when subjected to a humid, elevated temperature environment. It was also found that PAA surfaces are highly resistant to mechanical damage, but quite susceptible to grease contamination.</p>			

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**CHARACTERIZATION OF ALUMINUM SURFACES
PREPARED FOR ADHESIVE BONDING**

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Scanning transmission electron microscopy (STEM) and Auger/ESCA electron spectroscopy have been used to characterize changes that occur with handling and hydration on aluminum surfaces prepared for adhesive bonding.

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I. INTRODUCTION

This paper reviews some recent work at Martin Marietta Laboratories in which surface sensitive techniques such as scanning transmission electron microscopy (STEM) and Auger/ESCA electron spectroscopy have been used to characterize the surfaces of aluminum adherends prepared for adhesive bonding. The STEM is uniquely suited to this type of study because its ultra-high resolving power, when operated in the SEM mode (30 Å compared to 200 Å for a conventional SEM), allows the fine structure (~50 Å) of oxides on the adherends to be observed directly and evaluated for bonding purposes. The Auger/ESCA technique provides valuable information concerning surface chemistry and is an extremely powerful tool for detecting surface contaminants and degree of hydration of the surface.

In our work, we have employed these techniques in a complementary fashion to gain a basic understanding of the bonding mechanism and to identify contaminants that degrade bond strength. For example, we have shown in prior studies that:

1. Two commercially important pre-treatment process for aluminum adherends (the Forest Products Laboratory [FPL] process and the phosphoric acid anodize [PAA] process) are successful primarily because they provide an oxide structure on the Al surface which interlocks mechanically with the adhesive (or primer) to form a much stronger bond than would be possible if the oxide were smooth⁽¹⁾.
2. The presence of fluorine on these surfaces, which may be picked up from tap-water rinses, is extremely harmful because it results in a chemical reaction that removes the highly desirable oxide whiskers, thereby reducing the bond strength by as much as an order of magnitude⁽²⁾.

In more recent work we have extended these studies to investigate the effect of handling adherends which have been pre-treated with the PAA process, and some other factors that relate to bond durability as discussed below.

II. VULNERABILITY OF PAA SURFACES TO HANDLING

Using the high resolution capabilities of a JEOL-100CX STEM, operated in the SEM mode, we have demonstrated⁽¹⁾ that the PAA process yields an oxide structure that consists of well developed hexagonal cells from which protrude oxide whiskers as shown in Fig. 1. Such a surface is expected to be ideally suited for bonding because it can interlock with the adhesive or primer, to form a "fiber-reinforced interface." However, past experience has shown that precautions must be taken to avoid handling this type of surface prior to bonding⁽³⁾. In our recent studies we have investigated why handling degrades the bond strength of PAA surfaces⁽⁴⁾.

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Ever since an alert was issued by the PABST Program⁽³⁾ that PAA surfaces could not be handled prior to priming or bonding without risk of bond failures, questions have been raised whether handling served to damage the oxide mechanically, or to introduce contamination. Danforth and Sunderland's⁽⁵⁾ report concluded that both mechanical damage and contamination were responsible. However, since the SEM they used to look for mechanical damage did not have a resolving power adequate for viewing the fine oxide structures, we felt that the problem should be re-examined using the STEM.

To accomplish this, PAA treated surfaces were subjected to various "dirty" and "clean" handling techniques and then examined by STEM and Auger/ESCA. The results indicated that handling with bare fingers left a grease residue that completely covered the oxide allowing the underlying oxide whiskers to protrude in only a few regions, Fig. 2. Similar handling, but with a sheet of "off-the-shelf" aluminum foil placed between the fingers and the PAA surface also resulted in extensive grease contamination as observed by STEM and Auger. However, when the Al foil was first cleaned by etching in 0.1 N NaOH at 25°C, no evidence for any contamination or mechanical damage could be observed. Evidently, Al foil contains a film of grease, probably a residue from lubricants used in the rolling operation, which is sufficient to contaminate the PAA surface. When this is removed by etching, the PAA surface can be handled through the foil intermediary with no resulting effect on the surface at all.

These observations indicate that grease contamination, not mechanical damage to the oxide, is the principal degradation mechanism resulting from normal handling. Moreover, further studies showed that traditional "clean" handling techniques may not be clean enough to avoid contamination. For example, handling PAA surfaces with cotton or vinyl gloves, or between "clean" sheets of Kraft paper all resulted in some grease contamination, but no mechanical damage. In fact, throughout these studies we found that handling with etched Al foil was the only method tried that did not leave a grease residue.

The observation that the PAA oxide is not particularly susceptible to mechanical damage prompted us to determine what stress levels are required before damage becomes evident. Accordingly, samples were pressed between etched Al foils in a hydraulic press and examined by STEM. The results indicate that even when the stress was as high as 5000 psi, only "high" spots on the undulating Al surface suffered any significant damage. In these high spots it was evident that the oxide fingers had been crushed, but these regions constituted only a small fraction of the total surface area.

In summary, we have observed that the PAA surface is extremely resistant to mechanical damage, but is highly sensitive to grease pickup. Evidently, the microscopic surface roughness that is responsible for the success of this type of surface for bonding, causes it to retain grease, probably through capillary action. The full benefits of this highly desirable oxide morphology can be realized, however, if handling of the

bonding surface is avoided, or if contact is made only with truly clean materials such as etched Al foil. To complete the study, we are now evaluating the vulnerability of FPL surfaces to the same type of handling, and the efficiency of various processes that might be used to clean an accidentally contaminated surface.

III. CRYSTAL STRUCTURE OF OXIDES BEFORE AND AFTER HYDRATION

The crystal structure and degree of hydration of the oxide film on Al adherend surfaces are parameters that are expected to influence the durability of adhesive bonds. Bowen⁽⁶⁾ reported that the oxide film consists of two forms of crystalline hydrous oxide; a mechanically weak bayerite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and a strong boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$). This result has been used in many subsequent publications to assist in the interpretation of bond durability, etc., but our recent studies show that the result is not correct for properly prepared surfaces. In our studies we have used transmission electron diffraction, ultra-high resolution SEM, and Auger-ESCA to examine the structure of oxides on FPL, PAA and CAA treated surfaces.

Extensive electron diffraction studies on freshly prepared FPL and PAA stripped oxides have revealed no evidence for crystallinity in these surface films whatsoever. All the samples examined exhibited diffuse diffraction halos characteristic of an amorphous structure. To determine whether this amorphous structure is that of an aluminum oxide, or hydroxide, we have taken advantage of the fact that ESCA can be used to distinguish between the two compounds by measuring the chemical shift of oxygen. Thus, by comparing the shifts observed for Al_2O_3 and $\text{Al}(\text{OH})_3$ standards with those observed on FPL and PAA surfaces, it is possible to determine the degree of hydration or hydroxide formation. The results of this work indicate that the ESCA spectrum of surface films on freshly prepared samples are similar to the oxide standard, whereas if the adherends are subjected to a warm, moist or wet environment, the spectrum becomes similar to that of the hydroxide standard. (The precise conditions of temperature and humidity that give rise to the conversion will be discussed in a subsequent paper now in preparation.)

Electron diffraction and electron microscopy performed on some of the hydrated films show that they tend to be crystalline in nature and have a distinct morphology which makes them easy to recognize and distinguish from the original FPL, PAA or CAA oxides. For illustrative purposes we consider two extreme cases where i) a CAA surface, originally exhibiting a morphology of the type shown in Fig. 3, is subjected to a "sealing" operation consisting of immersion in boiling water for one-half hour, and ii) FPL treated adherends which, after adhesive bonding, are subjected to a wedge test at 150°F in 95% humidity.

The "sealed" CAA surface exhibits a morphology, Fig. 4, which, for obvious reasons, we have dubbed the "cornflake" structure. The surface

of adherends subjected to a humidity chamber wedge test in which the crack propagated along the adhesive/adherend interface, exhibits an identical structure as shown in Fig. 5. This morphology has been observed previously by Vedder and Vermilyea⁽⁷⁾ who used TEM and infrared spectroscopy to identify it as crystalline pseudo-boehmite, a material containing somewhat more water than perfectly crystallized boehmite. Our analysis, which indicates that the crystal structure is that of crystalline boehmite is consistent with that of Vedder and Vermilyea; we would not argue the point that it may contain somewhat more water than true boehmite. In any event, the distinct "cornflake" morphology, and the crystalline nature of the substance, appear to be characteristics of hydrated films that set them apart from films on freshly prepared adherends.

We conclude from this investigation that freshly prepared FPL or PAA adherends exhibit a surface film that is amorphous aluminum oxide, but that the oxide can be converted to crystalline boehmite (or pseudo-boehmite) when subjected to a humid, elevated temperature environment. We suggest that the material examined by Bowen⁽⁶⁾, which he claimed contained boehmite, may have been improperly prepared (using rinses or drying conditions at too high a temperature) or that the samples were stored improperly before examination. Further, we would like to point out that adherends which have been processed in such a way as to promote boehmite formation, may be undesirable for high performance bonding applications. Thus, even though the surface morphology shown in Fig. 5 exhibits a microscopic roughness which would lead to mechanical interlocking with the adhesive or primer, we have obtained preliminary evidence that the "cornflake" structure is not tightly bonded to the aluminum substrate. This conclusion is suggested by our observation that in wedge test specimens, the "cornflakes" are observed to preferentially stick to the adhesive, rather than to the aluminum substrate.

IV. CONCLUSIONS

In our continuing efforts to define those factors that are important in determining the performance and durability of adhesively bonded Al structures, we have attempted to resolve two controversial issues that needed clarification. First, we have shown that PAA surfaces are highly resistant to mechanical damage by normal handling procedures, but at the same time, are highly susceptible to grease contamination which is retained in the porous oxide structure. This conclusion is supported by studies performed using ultra-high resolution SEM, a technique which was not available to prior investigators who concluded that mechanical damage and grease retention were both problems with PAA surfaces⁽⁵⁾. It should be noted that our conclusion in no way suggests a criticism of the PAA surface, which, as we pointed out in a prior report⁽¹⁾, has highly desirable features for adhesive bonding applications. The present result does suggest, however, that sensible handling procedures are required if full advantage is to be taken of this type of surface.

The second issue considered in this paper regarding the crystal structure of films on Al adherends appears at first glance to be one that is of academic interest only. However, we wish to point out that there has been a very practical benefit from this study since it has demonstrated that the STEM can be used to readily distinguish between the original oxide and hydrated films simply on the basis of morphology. In the present study we have examined extreme cases, but we feel that all intermediate stages of hydration could be monitored in the same way. Such information, is expected to be of considerable benefit in studying the long term durability of adhesive bonded structures since bond strength is expected to be a very sensitive function of morphological changes that occur during hydration.

V. ACKNOWLEDGEMENTS

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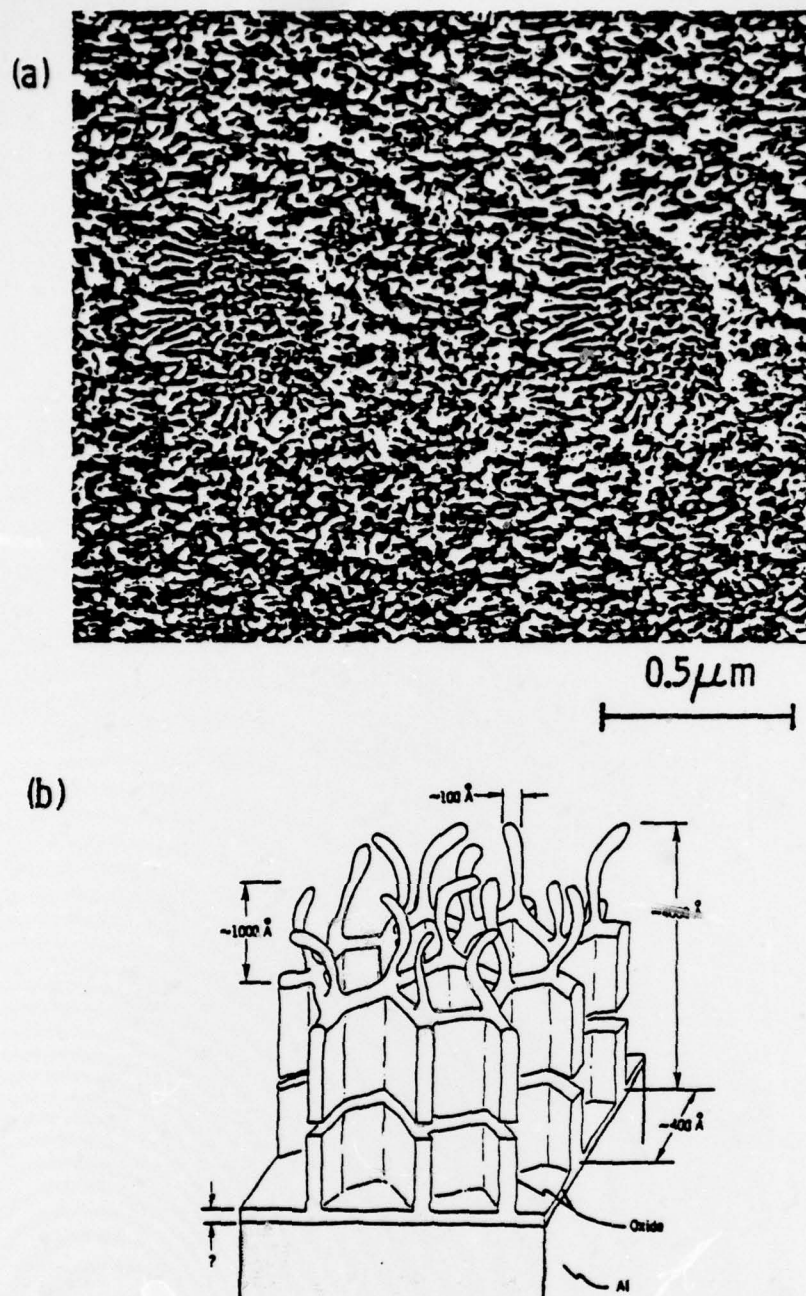


Figure 1. (a) Ultra-high resolution stereo SEM micrograph and (b) isometric drawing of the oxide morphology on a PAA treated aluminum surface. The origin of the depressed region in the oxide seen in (a) is unknown, but may have been due to a gas bubble whose presence inhibited oxide growth during anodization.

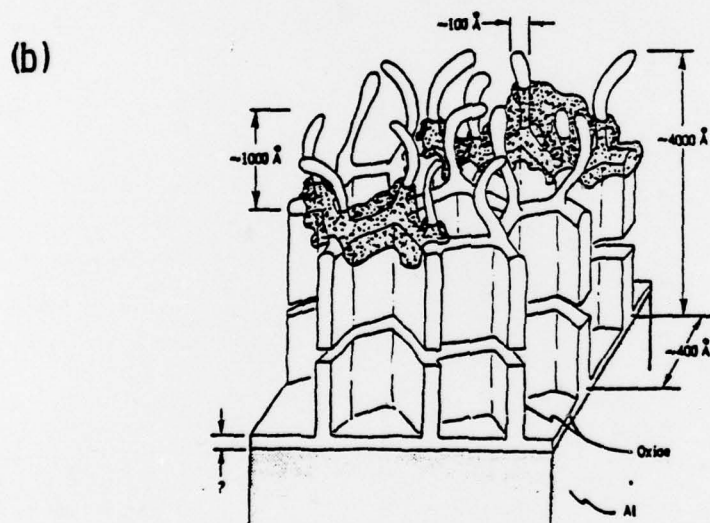
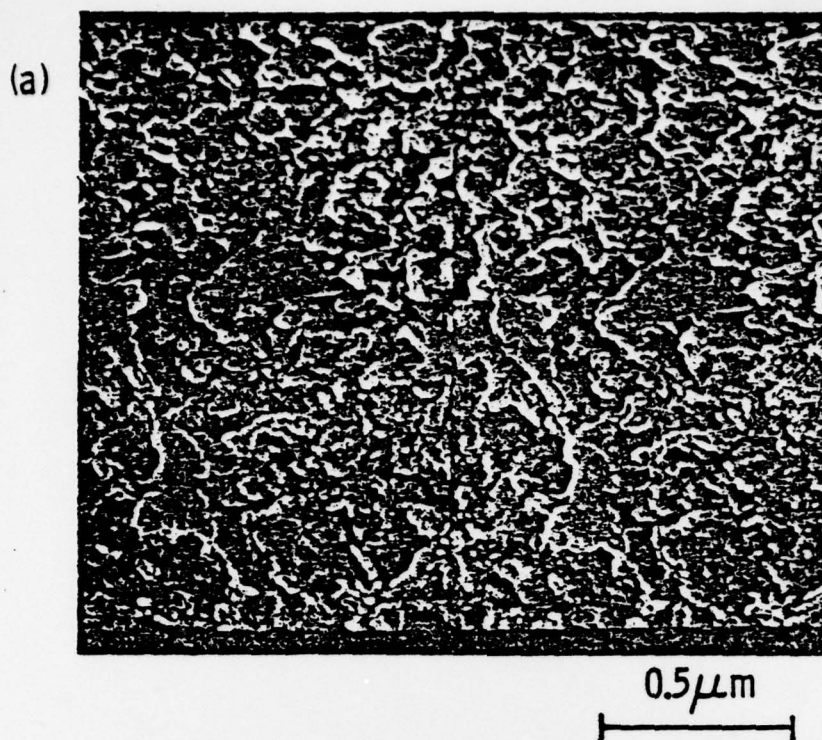


Figure 2. (a) Ultra-high resolution stereo SEM and (b) isometric drawing of a PAA surface after handling with bare fingers showing grease contamination.

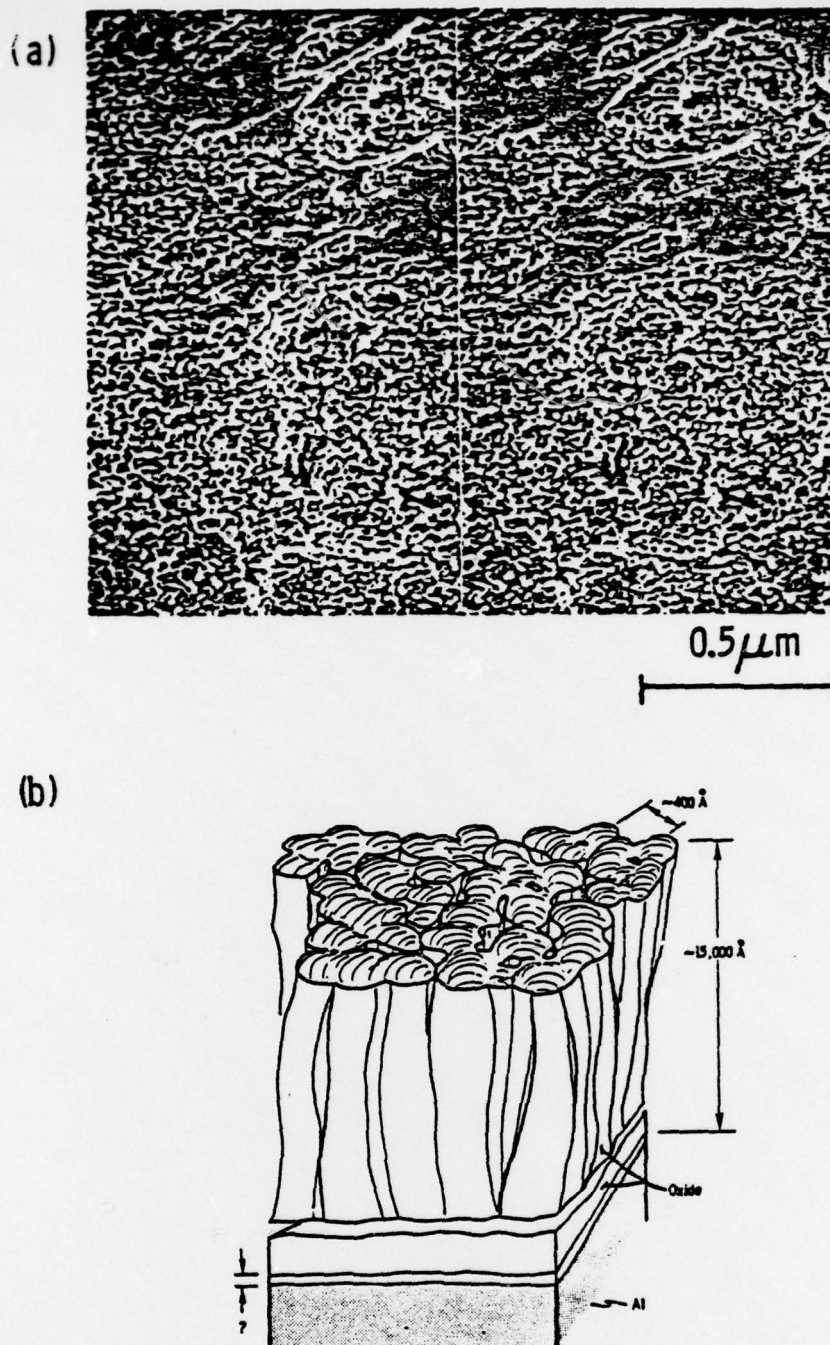


Figure 3. (a) Ultra-high resolution stereo SEM and (b) isometric drawing of the oxide morphology on Al surface treated with the chromic acid anodize (CAA) process.

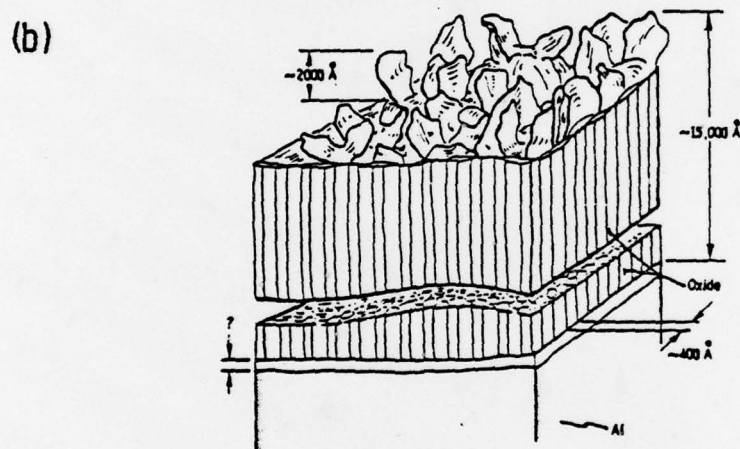
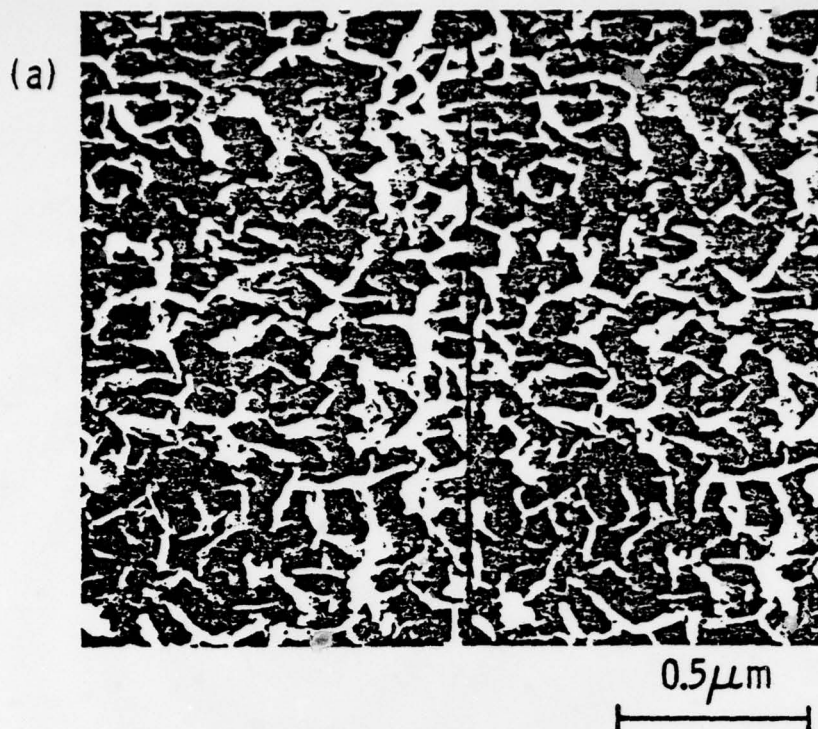


Figure 4. (a) Ultra-high resolution stereo SEM and (b) isometric drawing of a CAA surface after "sealing" showing hydroxide formation on upper surface.

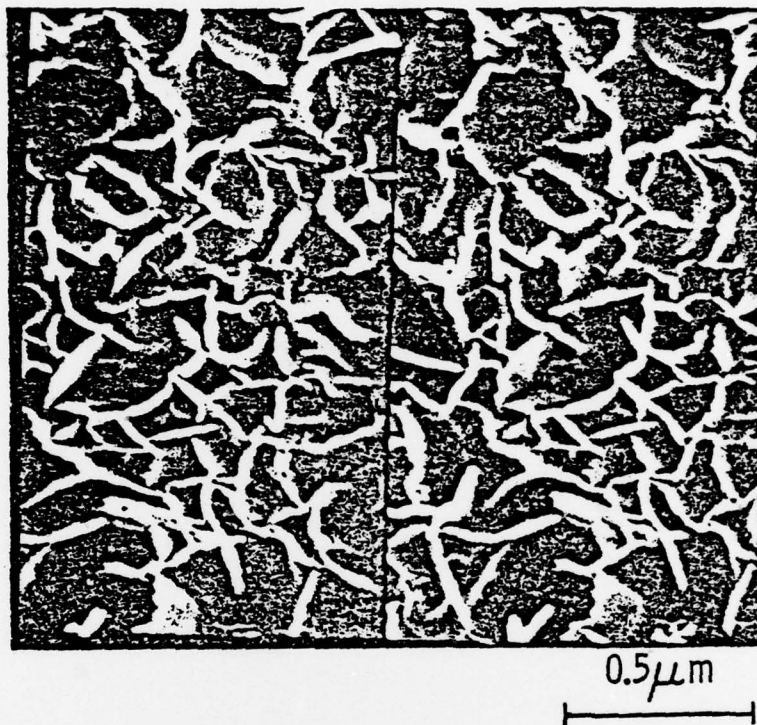


Figure 5. Ultra-high resolution stereo SEM of hydroxide morphology picked up on adhesive side of crack interface during a humidity wedge test.